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X-ray diffraction analysis of lattice defects of ZnSe thin films deposited at different substrate temperatures

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Abstract : The microstructural parameters of ZnSe thin films deposited at different substrate temperatures on glass substrates have been studied. ZnSe films produced by vacuum evaporation are polycrystalline sphalerite in structure with preferred orientation along (111) direction. The films are generally zinc deficient; but with increasing substrate temperature and thickness, stoichiometry improves greatly Variation of lattice parameter, average internal stress, grain size, microstrain and dislocation density with variation of substrate temperature and thickness have been reported

Keywords : ZnSe thin films, stoichiometry, microstructural parameters.

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1. Introduction

Zinc selenide (ZnSe) is an important compound semiconductor of II-VI family with zinc blende structure (a = 5.668 Å) and a direct band gap of 2.67 eV at room temperature [1]. ZnSe thin film has found potential applications in blue-green laser, light-emitting diodes, dielectric mirrors and filters, heterojunction solar cells and in other optoelectronic devices [2,3]. Although close-spaced vapour transport (CSVT) [4–7], liquid phase epitaxy (LPE) [8,9], molecular beam epitaxy (MBE) [10,11] and organometallic chemical vapour deposition (OMCVD) [12,13] are successfully applied for deposition of ZnSe on non-crystalline and single crystal substrates; physical vapour deposition (PVD) or vacuum evaporation [14–18] is also important because it gives good quality polycrystalline ZnSe thin films at relatively low cost.

For optimal performance of thin film devices, it is necessary for the films to have specific mechanical, optical and electronic properties which are again strongly dependent

on the film microstructure. Some of the important structural parameters which influence the device performance of thin films are (1) crystallinity, (2) phase structure, (3) lattice constant, (4) macro- and microstress, (5) grain size, (6) lattice faults and (7) surface or bulk chemical impurity. Microstructure of thin films is strongly affected by the nature of substrate and film deposition conditions like substrate temperature, deposition rate, residual gas pressure and angle of incidence of constituent vapour beams.

X-ray diffraction (XRD) method is the oldest but still most powerful technique of structural characterization of thin films. The experimental quantities that can be measured from XRD data are the angular position, total intensity, line width and line profile of Bragg reflection. It is well known that broadening of XRD profile is caused by occurrence of crystallites and existance of microstrains and faults in a crystalline material.

Evaluation of structural properties of evaporated ZnSe thin films has received little attention of researchers over the years. Raven and Kirk [14] reported the microstructure of ZnSe layers deposited on (100) Ge surface using transmission electron microscopy (TEM) and X-ray diffraction (XRD) method. At low substrate temperature, the films were polycrystalline with both cubic and wurtzite phase. The films became highly ordered when substrate temperature is raised. Thutupalli and Tomlin [15] found that ZnSe thin films (75–300 nm thick) on glass at room temperature were polycrystalline with cubic structure and films deposited at 373–673 K temperature range showed sharper X-ray diffraction with appearence of hexagonal phase. Aranovich *et al* [16] found that the apparent grain size of ZnSe thin films deposited on *p*-type GaAs and CdTe by co-evaporation of ZnSe, Zn and In or Ga (as dopant) in high vacuum (10^{-7} Torr) was nearly equal to the film thickness. El-Shazley *et al* [17] deposited ZnSe thin films on glass and mica substrates obliquely at 45° by evaporation with varying substrate temperature up to 423 K. ZnSe films on glass were found to be polycrystalline (cubic) with (111) preferred orientation. Crystallite sizes determined using X-ray broadening showed increase up to 423 K and then decreasing at 473 K and again increasing beyond 523 K. Electron microscopy diffraction showed existence of both cubic and hexagonal phases. ZnSe films deposited on mica also had peaks with mixed phase. Films deposited at room temperature when annealed, showed decrease in crystallite size upto 373 K and then slow increase. Pawlikowski [5] deposited thin films of ZnSe on glass and other substrates by close spaced vapour transport (CSVT) method at source temperature range 1043–1223 K and substrate temperature range 603–843 K. Resulting ZnSe films were found to be polycrystalline with (111) preferred orientation, independent of substrates used for deposition. Additional peaks corresponding to (311) and (220) orientations were frequently observed besides the main (111) peak. Dawar *et al* [6] deposited (111) oriented ZnSe thin films by a method similar to CSVT technique on glass substrates at around 623 K temperature. The grain size determined from Scherrer formula was found to increase with annealing in hydrogen atmosphere [7]. Rao and Islam [18] studied the structural properties of ZnSe thin films deposited on glass substrates by electron beam evaporation at room temperature. The films having thickness in the range 1–1.53 μm showed cubic polycrystals with (111) preferential

orientation. The crystallite size of ZnSe films estimated using Scherrer formula was 26 nm while lattice parameter was 5.676 Å.

Survey of the above mentioned works shows that studies of microstructural properties of evaporated ZnSe thin films have been few and those are also incomplete and qualitative in nature. In this paper, we present a detailed X-ray diffraction analysis of lattice defects of ZnSe thin films deposited on glass substrates at different substrate temperatures.

2. Experimental

Bulk ZnSe was synthesized from specpure (99.999%) constituent elements by fusion in an evacuated (~ 10^{-5} Torr) graphitized quartz ampoule. ZnSe thin films were deposited on microglass slides by vacuum evaporation of above mentioned ZnSe powder in high vacuum (pressure around 3×10^{-6} Torr). The source temperature was maintained at 1143 K and the source-to-substrate distance was fixed at 10 cm in all the depositions, while the substrate temperature T_{sub} was varied at 300 K (room temperature), 373 K, 473 K and 573 K. The details of evaporation technique had already been reported [19].

The thickness of the films was measured by dual-beam recording UV-VIS-NIR spectrophotometer (Shimadzu UV 2100, Japan) with photometric accuracy 0.3% T and wavelength accuracy 0.3 nm. The bulk composition of the films was determined by energy dispersive X-ray (EDX) analysis. The instrument used was the model CamScan series IIDV (UK) with Link AN 10000 super series AN 10/555 EDX microanalysis system. The accelerating potential was 15 kV. To avoid the presence of unwelcome elements due to interference of glass in the EDX analyses of ZnSe films, the sample films were peeled off from the glass substrates with epoxy resin pasted on it. The back surface of the film on glass substrate faced the electron beam as sample. Prior to loading in chamber, a thin carbon coating (~10 nm) was deposited on the films to avoid charging as the films were highly resistive in nature.

3. X-ray diffraction analysis

The X-ray line profiles from all the films including powder sample were recorded with the help of Philips (PW 1840) X-ray diffractometer using a copper target and nickel filter. The tube was operated at 40 kV and 20 mA. Care was taken to minimize instrumental broadening by using highly stabilized power supply, soller slits and appropriate slits to reduce divergence of X-ray beams. Routine check of the calibration and adjustments of the diffractometer was carried out with a standard silicon specimen. The scanning speed of the goniameter was maintained at 0.02° 2θ/sec.

3.1. Lattice parameter and average internal stress :

The d-spacing, characteristics of the symmetry and dimensions of unit cells, is determined from the angular position θ of the Bragg reflection in the diffraction profile by using Bragg formula :

$$2d \sin \theta = \lambda. \tag{1}$$

ZnSe is a cubic crystal, so its lattice parameter is given by

$$a = d\sqrt{h^2 + k^2 + l^2}. \tag{2}$$

A deviation of the measured lattice parameter from that of a strainfree bulk sample strongly indicates the presence of strain. The average internal stress S in the films can be determined using the following relation [20] :

$$S = (E_f / 2\gamma_f)[(a_0 - a) / a_0], \tag{3}$$

where a_0 is the lattice parameters of the bulk material, E_f is the Young's modulus and γ_f is the Poisson's ratio of the films. Here a refers to the lattice parameter perpendicular to the film plane. The values of E_f and γ_f used in calculation however, are those of the bulk material [21].

3.2. X-ray line broadening studies :

3.2.1. Background correction :

Background correction of the X-ray diffraction profiles is very important since the X-ray diffraction parameters *e.g.* integrated intensity, peak height, integral width, Fourier coefficient and variance of line profiles are affected differently by an improper choice of background level. Here, the background has been taken to be the mean of the two minima adjacent to the peak [22]. Background levels are adjusted for all the films properly taking the line profiles.

3.2.2. Integral breadth analysis

X-ray integrated intensity of the XRD line profile is essentially proportional to the area under the profile which is proportional to the amount of material lying in such a orientation that corresponding (*hkl*) planes are in Bragg reflection condition. The integral width is given by [23]

$$B = (I_p)^{-1} \int I(2\theta) d(2\theta), \tag{4}$$

where I_p is peak height and

$$\int I(2\theta) d(2\theta)$$

in the area of the XRD line profile after background correction. The area of the line profiles of all the ZnSe films deposited at different substrate temperatures were accurately determined after background correction.

The pure integral width (β) of the XRD line profiles were obtained by subtracting geometrical integral width (b) from observed integral width (B) of the films. The geometrical integral width (b) was determined from the XRD line profile of pure ZnSe powder formed in our laboratory.

3.2.3. Particle size and lattice strain

The pure integral width β was used to obtain the grain size D and microstrain ε assuming an exclusive contribution to broadening for either grain size or microstrain [24] :

$$D = K\lambda / \beta \cos\theta, \tag{5}$$

$$\varepsilon = (\beta \cos\theta)/4, \tag{6}$$

where the shape factor $K = 1$, θ is the Bragg angle and λ is the wavelength of X-ray radiation.

3.2.4. Dislocation density

The dislocation density ρ was calculated using the grain size and lattice strain values by the formula [25]

$$\rho = \left(3nK\varepsilon^2 / D^2 b^2 F\right)^{1/2}, \tag{7}$$

where n is the number of dislocations in a pile-up, K is a constant depending upon the strain contribution function, b is the Burgers vector of the dislocation and F is an interaction parameter. Assuming Cauchy strain profile for the XRD line profiles of ZnSe thin films, the value of K has been taken as 25 [24] and in the absence of extensive polygonization, we can assume, $n \equiv F$ and $b = d_{111} = a/\sqrt{3}$ [25]. Then the dislocation density becomes

$$\rho = 15\varepsilon / aD, \tag{8}$$

where a is the lattice parameter of ZnSe thin films.

4. Results and discussion

The structural characterization of ZnSe thin films were done for films in two thickness range 250–310 nm and 400–500 nm.

In the compositional analysis of ZnSe thin films by energy dispersive X-ray (EDX), a small amount (<0.5 atom%) of K and Fe were detected for a few samples along with Zn and Se. However, the normalized values of Zn and Se were considered for atomic percentage determination. The ZnSe thin films were generally zinc deficient. But we found the film stoichiometry improved greatly with increasing substrate temperature as evident from the results of EDX studies in Table 1 and plot of Figure 1. The ratio of Se to Zn atomic pecentage was always greater than one because the vapour pressure of Se is greater than that of Zn and their sticking coefficients are also different. But at higher substrate temperature, Se molecules are more reevaporated than Zn atoms and the sticking coefficient of Zn increases. So the adsorbed constituents recombine in proper ratio to form stoichiometric compound. So we got almost stoichiometric (Se/Zn atom% = 1.094) ZnSe thin films of thickness 410 nm deposited at 573 K.

XRD line profiles of ZnSe thin films deposited at different substrate temperatures showed a sharp single peak corresponding to (111) preferred orientation. However, no other

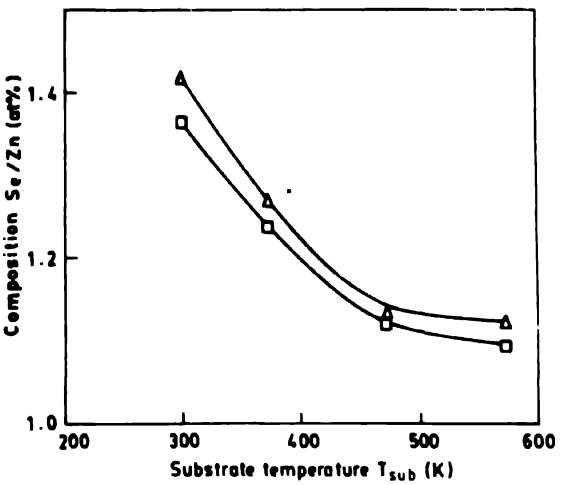

Figure 1. Variation of composition with substrate temperature for film thickness 250–310 nm (Δ), 400–500 nm (□).

Table 1. Microstructural parameters of evaporated ZnSe thin films

T_{sub} (K)	d (nm)	Se/Zn (at%)	a(Å)	$S(10^9)$ (dynes/cm^2)	Type	D(nm)	$\varepsilon(10^{-3})$	ρ (10^{11}/cm^2)
300	260	1 418	5.6631	0.2	Tensile	17	9.42	14 4
373	250	1 270	5.6631	0.2	Tensile	24	6.69	7 3
473	310	1.134	5.6866	5.2	Compressional	33	5.01	4.0
573	270	1.124	5.6825	4 2	Compressional	41	3.98	2.6
300	480	1.365	5.6580	1.4	Tensile	20	8.31	11 2
373	500	1.237	5.6682	0.9	Compressional	45	3.62	2.1
473	430	1.118	5 6784	3.3	Compressional	49	3.37	1.8
573	410	1 094	5.6743	2.3	Compressional	54	3.03	1.5

peak with measurable intensity from either ZnSe or the constituents was obtained in the X-ray diffraction trace. This proves that the ZnSe thin films were polycrystalline with zinc blende structure. The (111) direction is the close-packing direction of zinc blende structure.

The values of microstructural parameters namely lattice constant a, average internal stress S, grain size D, lattice strain ε and dislocation density ρ for ZnSe thin films of different thickness range deposited at various substrate temperatures, are shown in Table 1.

Also the variation of these quantities with substrate temperature T_{sub} is also shown in Figures 2–6.

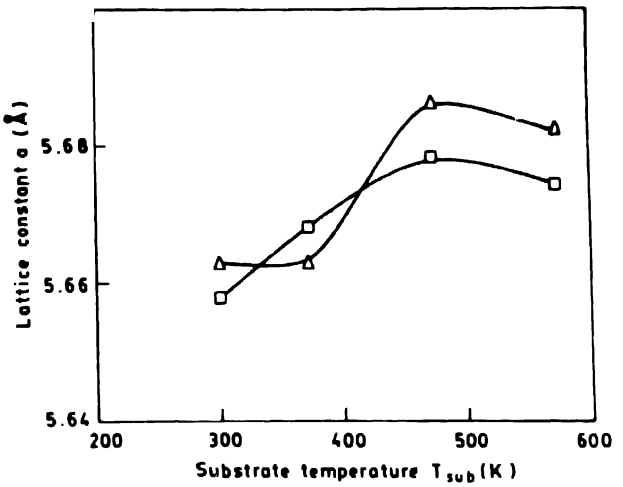

Figure 2. Variation of lattice constant with substrate temperature for film thickness : 250–310 nm (Δ), 400–500 nm (□).

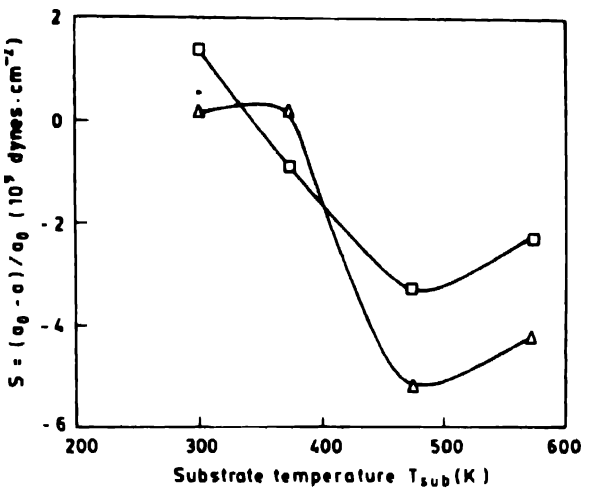

Figure 3. Variation of average internal stress with substrate temperature for film thickness . 250–310 nm (Δ), 400–500 nm (□).

ZnSe thin films deposited at and below 373 K did not stick well to the glass substrates whereas films adhered to the glass slides when grown at T_{sub} = 473 K and 573 K.

The lattice parameter of ZnSe thin films first increased abruptly and then decreased to some extent with increase in substrate temperature (Figure 2). The average internal stress of ZnSe thin films was tensile for room temperature (300 K) deposited

films, but it changed to compressional stress—first increasing, coming to a peak and then decreasing nominally as films were deposited at increasing substrate temperature (Figure 3). The thermal stress [20] developed was only within 10% of average internal stress and was therefore neglected.

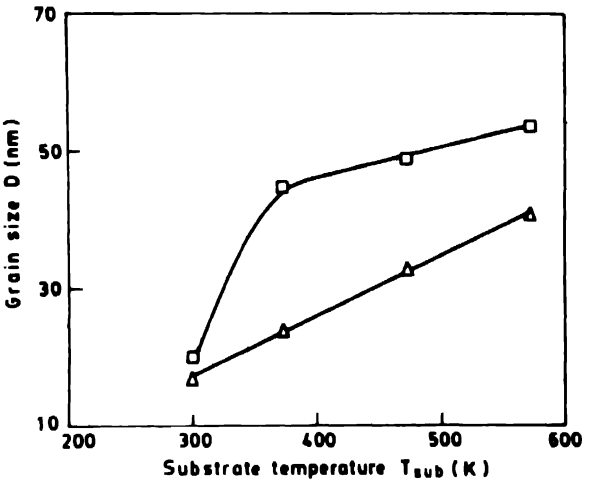

Figure 4. Variation of grain size with substrate temperature for film thickness . 250–310 nm (Δ), 400–500 nm (□)

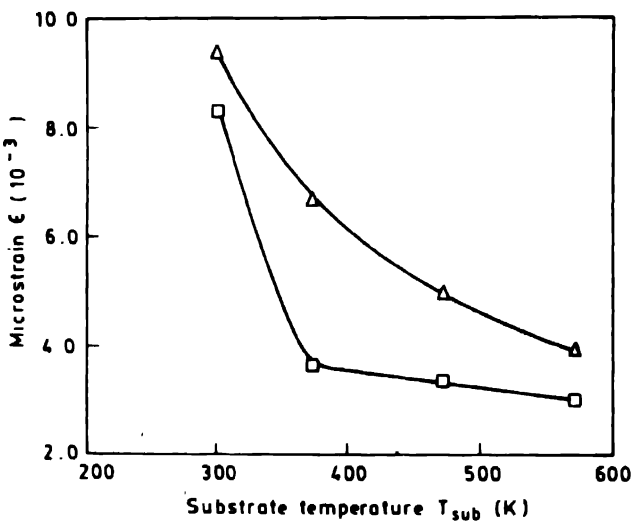

Figure 5. Variation of microstrain with substrate temperature for film thickness : 250–310 nm (Δ), 400–500 nm (□).

The grain size increased first abruptly and then slowly for increase in T_{sub} (Figure 4), while both microstrain and dislocation density followed opposite behaviour—decreasing first abruptly and then slowly for increase in T_{sub} (Figures 5 and 6).

Possibly recrystallization through diffusion in the disordered regions of the films occurs during the deposition of ZnSe at increasing substrate temperatures and correspondingly microstructural parameters of the ZnSe thin films change abruptly. But at

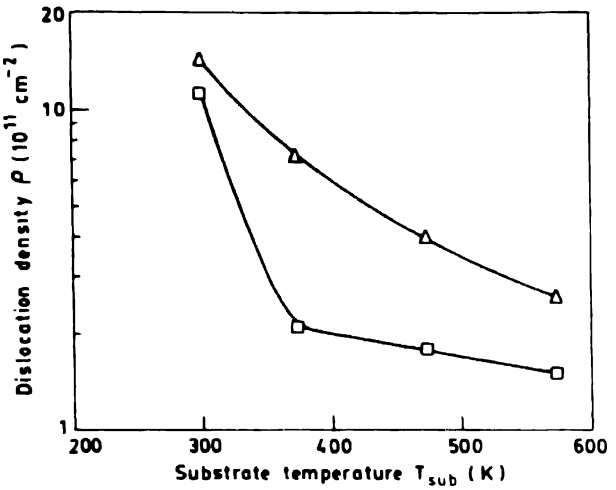

Figure 6. Variation of dislocation density with substrate temperature for film thickness 250–310 nm (Δ), 400–500 nm (□).

still higher substrate temperatures, re-evaporation of the constituent atoms and molecules occurs from the ZnSe film surface. When there is a balance between the two opposite processes, microstructural parameters change more slowly.

5. Conclusion

In the present study, it is observed that XRD line profiles of ZnSe thin films of different thickness range deposited at various substrate temperatures show a single peak corresponding to (111) line of ZnSe. No separate peaks for Se or Zn or any other phase are obtained in the X-ray diffraction traces. This proves the films are polycrystalline sphalerite in structure with preferred orientation along (111) direction. ZnSe films deposited above 373 K adhere well to the glass substrates. The films are generally zinc deficient; but with increasing substrate temperature and thickness, stoichiometry improves greatly. The grain size increases with increase in substrate temperature and film thickness. Lattice strain and dislocation density both decrease when substrate temperature and film thickness increase. The average internal stress is tensile for room temperature deposited films, but it becomes compressional when substrate temperature is increased.

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